

## THE CATALYTIC ACTIVITY OF Fe/ZSM-5 FOR HYDROCARBON SYNTHESIS AND EXAFS STUDY OF ITS STRUCTURE

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### INTRODUCTION

Hydrogenation of carbon dioxide has been paid more and more attention recently because of its green house effect and for synthesis of hydrocarbons and alcohols<sup>1,2</sup>. Unfortunately, it was observed that carbon dioxide can be converted into only carbon monoxide and methane over the many effective Fisher-Tropsch catalysts. The selectivities forming more than C<sub>2</sub> hydrocarbons and alcohols on them are, if any, very low<sup>3</sup>. In the recent years, Fe, Rh and other catalysts supported on suitable carriers and having some promoters were found to have high selectivities for C<sub>2</sub>-C<sub>4</sub> hydrocarbons under high pressures<sup>4,5</sup>. Some studies of adsorption of CO<sub>2</sub> by IR and the catalytical reaction kinetics under different temperatures and pressures were also reported<sup>6,7</sup>. All these researches have given great contribution to develop the catalytic conversion process of carbon dioxide to match the requirement of human environment protection and new energy source.

In this paper it is reported that the Fe/ZSM-5 has good selectivity to C<sub>2</sub>-C<sub>4</sub> in the hydrogenation of CO<sub>2</sub> and EXAFS study shows the change of the local environment of Fe on the catalyst during the deactivation process.

### EXPERIMENTAL

Preparation of catalysts: The weighed amount of metal nitrate, such as 2.93 g ferric nitrate, was dissolved in water to make a diluted solution in which 5.0 g support, HZSM-5 zeolite, was added. It stands in room temperature for two hrs by frequently stirring and dried at 393K for 10 hrs. The impregnated precursor was calcined at 723K, 2 hrs in flow of 40 ml/min of air, and cooled to room temperature to get the oxidized state of

the catalyst, 7.5% Fe/ZSM-5. It was reduced in a stainless steel reactor in hydrogen at 773K, for 4 hrs before hydrogenation of CO<sub>2</sub>.

**Hydrogenation:** The activity of the catalysts was determined in a flow system at space rate, 6000 ml/g.h with CO<sub>2</sub>:H<sub>2</sub>=1:4 at different temperatures between 500 to 650K and under 1-20 atmospheric pressures. The products were analyzed by a gas chromatographic system with HFD and TCD as detectors for hydrocarbons and the gases.

**X-ray absorption:** The X-ray absorption experiments were performed on Rigaku, 6KVA anode-rotating X-ray machine. The photon intensity was recorded with a solid detector and TP-801 monitor. All data analysis was carried out with EXAFS program on IBM-PC computer. The fitting was done using experimentally determined Fe-O and Fe-Fe phase shifts and backscattering amplitudes.

## RESULTS AND DISCUSSION

### 1. The effects of supports on activity and selectivities

The same amounts of Fe, such as 15%, were supported on SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, HZSM-5, Cr<sub>2</sub>O<sub>3</sub>, Nb<sub>2</sub>O<sub>5</sub> and La<sub>2</sub>O<sub>3</sub> individually by impregnation, calcination and then reduction at 773K, in H<sub>2</sub>, for 4 hrs. The hydrogenation activity and selectivities were measured in the flow system at 600K, 6000 ml/g.h of the reactant mixture of CO<sub>2</sub>:H<sub>2</sub>=1:4. The activity expressed as the percentage of conversion of CO<sub>2</sub> and the selectivities as percents of the converted CO<sub>2</sub> are listed in Table 1. From the data it can be seen that the properties of supports affect conversion of CO<sub>2</sub> very seriously, HZSM-5 made the Fe catalyst active 50 time more than that on La<sub>2</sub>O<sub>3</sub> and the selectivity forming C<sub>2</sub>+C<sub>3</sub> can reaches to 33.2% on Fe/ZSM-5, only about 1% on Fe/SiO<sub>2</sub>, Fe/Al<sub>2</sub>O<sub>3</sub> and Fe/Cr<sub>2</sub>O<sub>3</sub> and even nothing on Fe/La<sub>2</sub>O<sub>3</sub>. The better effect of Nb<sub>2</sub>O<sub>5</sub> on the C<sub>2</sub>+C<sub>3</sub> selectivities is in agreement with that reported in the literature<sup>8</sup>.

### 2.Loading of Fe on HZSM-5 and its effects on catalytic properties

The results listed in Table 2 indicate that the activity and C<sub>2</sub> and C<sub>3</sub> selectivities gradually increase by loading more and more Fe until 30% on the support. XRD experiments demonstrate that the increasing loading of

Fe resulted in the growing up of Fe particles on the reduced catalysts from 170 to 310Å (average particle diameter) from 5 to 30% Fe on HZSM-5. It can also be seen from Table 2 that the changes of C<sub>2</sub> and C<sub>3</sub> selectivities parallel with each other for loading more Fe and rising reaction temperatures. These results show that the metal Fe surface plays the main role in the hydrogenation of carbon dioxide and for growing of the C-C chains. In this particle size range, the larger, the particle of metal Fe, the better, the catalytical reactivity.

### 3. The effects of some promoters

Addition of 2.5% Cu, Ni, Ru, Rh, Co, the easily reduced metals to 15%Fe/ZSM-5 increase the activity and C<sub>2</sub>, C<sub>3</sub> selectivities at high reaction temperatures. At 650K the conversion of CO<sub>2</sub> reached 30.1% over Fe-Ru/ZSM-5 and CO, CH<sub>4</sub>, C<sub>2</sub>, C<sub>3</sub> and C<sub>4</sub> selectivities are 30.5, 27.7, 20.8, 14.0 and 7.0 respectively, that is, hydrocarbons become the main products, C<sub>2</sub>+C<sub>3</sub>+C<sub>4</sub>, 41.8% besides 27.7% CH<sub>4</sub> and CO only 30.5%. Promoter, Ni lets methane to be the main hydrogenation product, 51.5% in 4.1% converted CO<sub>2</sub> at 550K. However at 650K, C<sub>2</sub>+C<sub>3</sub> hydrocarbons reach to 21.7% , methane 22.9% and CO, 45.4% in 31.5 % converted CO<sub>2</sub>. As shown in the author's TPR experiments<sup>9</sup>, Ni and Ru could move the reduction peak temperatures of Fe<sub>2</sub>O<sub>3</sub> to the lower positions, that is, they could promote the reduction of Fe to metal state which is necessary to catalytical hydrogenation of CO<sub>2</sub> over Fe catalysts.

Na<sub>2</sub>O and MgO and other alkaline and alkaline earth metal oxides can increase a little bit of the hydrogenation activity, however, decrease the C<sub>2</sub> selectivity. They can inhibit the growing of C-C chain making methane as the main products<sup>10</sup>.

The transition metal oxides, such as V<sub>2</sub>O<sub>5</sub>, MoO<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub> decrease both the hydrogenation activity and C<sub>2</sub>, C<sub>3</sub> selectivities a lot at low reaction temperatures. In comparison with Fe/ZSM-5, these promoted catalysts have great temperature dependence. At 650K they have a comparable activity to that over Fe/ZSM-5 except the lower selectivities. These phenomena could be related to the inhibition effect to reduction of FeO and this effect would decline at the temperatures as higher as 650K.

### 4. Stability of the catalysts

In Fig.1 the hydrogenation activity and C<sub>1</sub>, C<sub>2</sub> and C<sub>3</sub> selectivities on Fe/ZSM-5, Fe-Cu/ZSM-5, Fe-Ru/ZSM-5, Fe-Cr/ZSM-5 and Fe-Cu-Ru/ZSM-5 were plotted against the reaction time. Although the initial activities on Fe/ZSM-5 and Fe-Cu/ZSM-5 are very high and reach the maxima after 1 hour, they drop very quickly later. After 5 hrs, the selectivities forming C<sub>1</sub>, C<sub>2</sub> and C<sub>3</sub> gradually decrease to the lowest values. On the contrary, the effect of Ru is very interesting. Over Fe-Cu-Ru/ZSM-5 the selectivities of C<sub>2</sub> and C<sub>3</sub> keep increasing with reaction time at expense of that of methane when the conversion of CO<sub>2</sub> gradually increases to a stable level, around 10%. After 10 hrs, selectivities of C<sub>1</sub>, C<sub>2</sub> and C<sub>3</sub> reach to 38.0, 19.0 and 16.5% respectively. It seems that the active centers which favor to growing of C-C chains were formed with reaction time instead of that for methane. The co-promoters, Cu-Ru, make Fe-Cu-Ru/ZSM-5 the best hydrocarbon synthesis catalyst from CO<sub>2</sub> and H<sub>2</sub> under our experimental conditions.

## 5. EXAFS study of the structure of the catalysts

EXAFS as a powerful tool has been widely used for study of the structure of catalysts.<sup>12</sup> The data obtained by fitting the filtrated  $k^2 \cdot x(k)$  with models of Fe-C and Fe-Fe for the Fe local environments of different catalysts at the different reaction times are listed in Table 3. The Radial Structure Functions (RSF) of Fe in Fe/ZSM-5 catalyst measured after 0.5, 2.0 and 24h are shown in Fig.2. It can be seen from Table 3 that the new Fe-C coordination was formed in the deactivated Fe- and Fe-Cu catalysts, the coordination numbers of nearest Fe around Fe centers decrease with time from 7.5 and 8.5 (0h) to 2.5 and 3.0 (24h) and a farther Fe-Fe formed.

From Fig.2 we can see that the peak height of Fe-Fe obviously decrease with time if we know the different Y-scales in the three figures from 40 (0h) to 20 (24h) being used and the large noise level in the third figure. The Fe-Fe interaction was interrupted by the carbon atoms which enter between iron atoms and some kind of Fe-C species are formed owing to the deposit of the carbon atoms on the surface during the reaction process. All these caused the deactivation of the catalysts. On Fe-Cu-Ru/ZSM-5, Fe-Fe coordination number almost does not change comparing 7.0 after 24h to 7.5 for 0h Fe/ZSM-5 and at the same time only 0.4 carbon atoms approach to Fe atoms on Fe-Cu-Ru/ZSM-5 comparing 2.5 on Fe/ZSM-5. It is known that Cu can inhibit the deposit of inactive carbon on Fe surface<sup>13</sup>. The better activity and stability of the Fe-Cu-Ru/ZSM-5 than

that of the others can be explained from the viewpoint of the local structure of Fe on the catalysts by EXAFS study.

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Table1 Effects of Supports on the Activity and Selectivities

Support	Conv. %	Selectivity, %				
		CO	CH <sub>4</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>2</sub> +C <sub>3</sub>
SiO <sub>2</sub>	2.3	89.9	8.9	1.2	0.0	1.2
Al <sub>2</sub> O <sub>3</sub>	6.4	98.0	1.4	0.4	0.1	0.5
HZSM-5	15.1	43.6	23.2	14.8	18.4	33.2
Cr <sub>2</sub> O <sub>3</sub>	5.2	92.2	6.5	1.0	0.3	1.3
Nb <sub>2</sub> O <sub>5</sub>	5.4	74.6	17.9	4.3	3.2	7.5
La <sub>2</sub> O <sub>3</sub>	0.3	95.2	4.7	0.0	0.0	0.0

Table 2 The Effects of Loading of Fe

Content %	Temp. K	Conv. %	Selectivity %				
			CO	CH <sub>4</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>4</sub>
1.0	600	1.5	97.0	3.0	0.0	0.0	0.0
	650	5.1	98.8	1.0	0.2	0.0	0.0
5.0	550	1.8	82.0	16.4	1.6	0.0	0.0
	600	6.4	83.7	12.4	3.1	0.8	0.0
	650	11.5	88.8	8.5	2.4	0.3	0.0
7.5	550	2.5	76.8	17.9	2.3	1.2	0.5
	600	6.8	73.1	16.8	5.3	2.6	0.7
	650	5.5	71.5	14.9	6.7	3.2	0.2
15.0	500	1.2	85.0	12.0	2.0	1.0	0.0
	550	3.9	60.0	21.6	6.8	7.6	6.4
	600	5.1	43.6	23.2	14.8	12.0	6.4
	650	30.5	65.1	16.0	9.6	6.8	1.9
30.0	500	1.5	79.6	9.6	3.4	5.4	2.0
	550	5.3	67.3	13.5	5.7	5.6	7.9
	600	25.7	42.6	17.4	13.0	12.8	14.2
	650	39.4	53.8	16.7	12.0	11.4	6.1
60.0	500	3.0	82.9	12.3	1.7	1.7	1.4
	550	11.9	58.5	15.7	8.4	10.5	8.9
	600	27.7	36.9	16.9	11.9	16.7	17.6
	650	35.7	63.2	14.5	9.4	8.3	4.6

Table 3 EXAFS Results of the Catalysts

Catalyst	Bond	Reaction Time (h)			
		0.0	0.5	2.0	24
15%Fe	Fe-C R		2.00	2.00	1.90
			0.5	1.5	2.5
	Fe-Fe R	2.49	2.51	2.55	2.48
		7.5	6.0	5.0	2.5
	Fe-Fe R			2.60	2.65
				2.5	3.8
15%Fe,10%Cu	Fe-C R		2.00	2.00	1.87
			0.7	1.5	2.0
	Fe-Fe R	2.50	2.52	2.50	2.48
		8.5	7.5	4.0	3.0
	Fe-Fe R			2.60	2.65
				2.5	5.0
15%Fe,10%Cu 2.5%Ru	Fe-C R			2.00	2.00
				0.3	0.4
	Fe-Fe R			2.5	2.5
				8.0	7.0

Notes: All catalysts were supported on HZSM-5. The unit of R is Å. CN-coordination number.

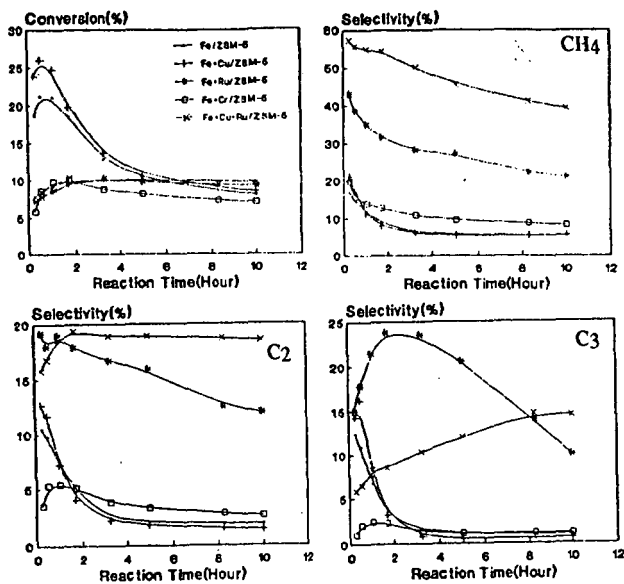


Fig.1 The relationship between the hydrogenation activity, selectivities and reaction time over several catalysts.

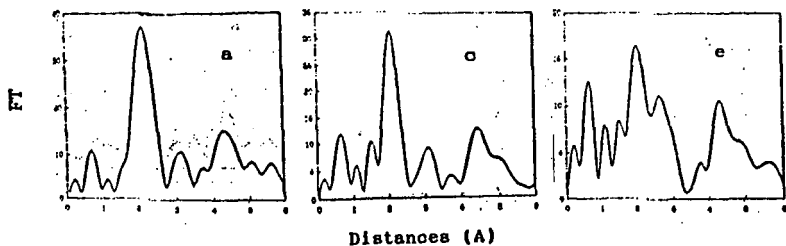


Fig.2 The RSFs of Fe measured at different reaction time. a-0.5h, c-2h and e-24h. The main peak at around 2.5Å is from the Fe-Fe coordination in Fe/ZSM-5.